CHARACTERISATION OF BIODIESEL PRODUCED FROM CASTOR OIL

MOHAMAD NADZRIE BIN LARY

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2014

ABSTRACT

Ricinus communis L., or also well-known as castor bean plant which belong to *Euphorbiacceae* family, contain 35% - 55% of oil when extracted. This castor oil contained high value of fatty acid or ricinoleic, which make transesterification process become easier due to high solubility in methanol. Castor oil also reported slowly becoming one of valuable chemical feedstocks because of its special characteristic. Besides, production of biodiesel also gained from castor oil.

Biodiesel produced from castor oil has been one of important research for current researcher. Many of them successfully produced biodiesel with several methods and different catalyst as the cheapest method still the major target. This research focus on using calcium oxide (CaO) as the catalyst which is a type of heterogeneous catalyst. Usage of heterogeneous catalyst seem to help a lot in saving the production cost. To ensure the product can be used or not, the produced biodiesel will be characterized and compare with the standards and result from previous researcher on castor oil. ASTM D6751 standards is the reference during the characterisation part take place.

ABSTRAK

Ricinus communis L., atau lebih dikenali sebagai pokok castor yang terdiri daripada kumpulan tumbuhan keluarga *Euphorbiacceae*, mengandungi 35% - 55% minyak apabila di extrak. Minyak castor ini mengandungi asid lemak dan asid ricinoleic yang tinggi, membuatkan proses transesterifikasi lebih mudah kerana kelarutan yang tinggi dalam methanol. Minyak castor juga dilaporkan mula menjadi stok bahan mentah yang berharga disebabkan oleh keistimewaan sifatnya. Malahan, pengeluaran biodiesel juga diperolehi daripada minyak castor.

Biodiesel yang dihasilkan daripada minyak castor telah menjadi salah satu kajian yang penting bagi penyelidik masa kini. Ramai di Antara mereka yang telah Berjaya menghasilkan biodiesel melalui pelbagai kaedah dan pelbagai pemangkin, namun kaedah yang termurah masih menjadi sasaran utama. Kertas kerja ini memfokuskan atas penggunaan kalsium oksida sebagai pemangkin yang merupakan sejenis pemangkin heterogen. Penggunaan pemangkin heterogen membantu dalam penjimatan kos penghasilan. Untuk memastikan hasil penghasilan boleh digunakan, biodiesel yang dihasilkan akan dipastikan ciri-ciri menepati piawai dan dibandingkan dengan hasil penyelidik seblemun ini. Piawaian ASTM D6751 akan digunakan sebagai rujukan semasa pencirian dilakukan.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Motivation and problem statement

The World Energy Forum 2012 suggested the fossil-oil would be distinct in less than ten decades. Searching for new and renewable energy is the most essential nowadays in order to retain the usage of fuel-engine equipment and transportation. Biofuel, such as biodiesel is one of the alternative idea to replace fossil fuel in current situation. Biodiesel can be mixed with petro fuel and give lower exhaust emission. In addition, it is very important to have green energy as it could help having better and clean environment. Furthermore, using bio-plant lead to good sustainability because crop can be plant and grow at almost everywhere without having extinction, also the price of biofuel is much cheaper than fossil-based oil.

Castor Bean and Castor Oil

Biodiesel can be produced from various type of vegetable oil. One of it is castor oil which extracted from castor bean. Ricinus communis L. or famously known as castor bean plant is a type of plant that belong to Euphorbiacceae family. This plant originally found in Africa but also could be found wild in the tropical and subtropical countries all around the world. Due to wild conditions of this plant, its well-adapted to arid conditions and anti-cyclonic condition which also able to stand long period of drought (Ferrero, 2006). Nowadays it widely grown on large and wide scale as commercial crop for its oil. The oil content inside the bean were approximately in range from 35% - 55%, depending of the seed and environment of the seed being planted. Handling of this bean must give a great care because fungus could grow on the beans if expose to certain temperature and humidity.

Castor oil is colourless to pale yellow and without any taste or odour. Chemically, it is triglyceride contained approximately 90% of fatty acid or ricinoleic. Others than that, it also contain of oleic and linoleic acids. Ricinoleic acid, a monounsaturated with 18-carbon fatty acid has hydroxyl functional group on the twelfth carbon. Due to this unusual cases make castor oil and ricinoleic acid becoming one of valuable chemical feedstocks (Chakrabarti and Ahmad, 2008). Besides that, biodiesel produced from castor oil is low cost compared to production of biodiesel from other oils regarding to its solvability in alcohol transesterification could occur without usage of many excess heating equipment (Conceicao, et al., 2007).

Biodiesel

Recently, biodiesel getting high demand, and getting higher interest when the production is involving lower and cheaper cost. It define as any diesel equivalent ester produced by transesterification process from biological material which are edible and non-edible oil. Chemically, biodiesel knows as "Free Fatty Acid Methyl Ester" (Sreenivas, 2011). Biodiesel is biodegradable and nontoxic fuel. Forero (2006) conclude in his journal that castor oil biodiesel can be used as petroleum diesel additive that improving in both environmental and flow of the petroleum fuel. In August 10, 1983, about hundreds years ago, Rudolf Diesel first to test peanut oil as fuel for his engine. Biodiesel does not contain any petroleum, but it can be blend with any level of petroleum diesel to produce biodiesel blend (Deshpande, et al., 2012). However, pure biodiesel cannot be injected to diesel engine vehicle and need several modification need to be done to the diesel engine in order fit the requirement to use the pure biodiesel. Furthermore, it also can lead to corrosion in vehicle material and later fuel system blockage, filter clogging, seal failures and deposits at injection pumps. Use in internal combustion could cause engine durability problems. All those problem occurs when we inject pure biodiesel inside the diesel engine vehicles (Atabani, et al., 2012).

Transesterification

For producing biodiesel, transesterification process is one of the most suitable method to be used because castor oil has high viscosity relatively to vegetable oils. Gerpen and Knothe (2005) wrote that there are possible four methods to reduce the high viscosity of vegetable oils to enable their use in common diesel engines without having any operational problems. The four methods are blending with petrodiesel, pyrolysis, microemulsification and transesterification. We are focusing on transesterification process because it was found that up to 85% of ester could be obtained (Chakrabarti and Ahmad, 2008). In the transesterification process, triglyceride component inside the castor oil will react with alcohol with presence of catalyst, then will produced glycerol and methyl ester.

Catalyst

From most of the experiment that has been conducted by previous researcher, same reaction used using homogenous catalyst such as potassium and sodium hydroxide, sodium and potassium alkoxides. Besides, by using those catalyst shows the reaction is faster than acid catalyst such as sulfuric acid, hydrochloric and sulfonic acid (Fukuda et al., 2001; Ma and Hanna, 1999). Although having aimed reaction by using the homogenous catalyst, there main disadvantages of the aforementioned homogeneous catalysts that is the undesirable production of both, glycerol and soap. This will increase the production cost as also the catalysts consumed thus reducing the efficiency of the catalyst (Romero, et. al, 2011). In the other hand, usage of heterogeneous catalyst inside the biodiesel production could save the production cost. Advantages of using heterogeneous catalyst are it does not leave neutralization salts in the glycerol produced and can be retained in the reactor by filtration. Regarding to the circumstances, induction to the heterogeneous catalyst could help reducing the cost compare by using the homogeneous catalyst. Neutralization salt in the glycerol does not leave by the heterogeneous catalyst and retained in the reactor by filtration process. Furthermore, number of separation can be decrease as additional neutralization stage does not required (MacLeod, et al., 2007). In addition, heterogeneous catalyst is less corrosive, and can be

used in fixed-bed reactor, that much more safe, cheaper, and more friendly to environment (Dossin, et al., 2006).

Problem Statement

High interest and high demand for biodiesel in the world market has increase the interest among researcher to find the best method for producing the biodiesel. Furthermore, biodiesel with much lower and cheaper cost has been the major target among the researcher as most of investor targeting on much lower cost but high grade biodiesel. Biodiesel itself does not contain any petroleum but can be blend with the petroleum fuel. Several automotive modification will be needed to be done before the pure biodiesel can be used with the automotive engine.

By using castor oil, with considering the current production and plantation of the castor plant, castor has capability to contribute toward production of biodiesel which is renewable energy. This research aiming to produce biodiesel through transesterification reaction with the use of heterogeneous catalyst. Compared to previous research where homogeneous catalyst has been used to enhance the reaction, this research would introduce the use of heterogeneous catalyst because of the price as heterogeneous catalyst is much cheaper than homogeneous catalyst, and efficiency of homogeneous will decrease as the catalyst was consumed by the reaction.

1.2 Objectives

The target of this research are:

- To produce biodiesel from castor oil transesterification using calcium oxide (CaO) catalyst.
- To characterise the biodiesel produced from castor oil.

1.3 Research Scope

The following are the scope of this research:

i) Experimental work on producing biodiesel through transesterification process with heterogeneous catalyst.

ii) Experimental analysis and characterisation analysis of produced biodiesel.

1.4 Main contribution of this work

The following are the contributions of this work:

- Biodiesel as substitute fuel to replace petroleum diesel
- Producing low cost biodiesel

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides an introduction of the thesis and what will be do along the research paper. This chapter explaining the detail explanation on the selection of castor oil as the main component of the transesterification process, and the origin of the oil. To produce the desired biodiesel, transesterification reaction will be used with the reason of the usage of heterogeneous inside the reaction. The selection of ratio of methanol-catalyst and oil for the transesterification process do affect the result of the produced biodiesel. Besides, the catalyst weight percentage also need to be considered.

Chapter 3 review the research methodology for this experiment. The castor oil will need to undergo transesterification process to produced targeted biodiesel. The transesterification is one of the best method to produce biodiesel from feedstock vegetable oil. To ensure transesterification is run on the best condition, several suggestion used based on suggested by previous researcher. The best of 6:1 molar ratio between methanol-catalyst and oil ratio is used, under system temperature of 60-70 ^{o}C and around 200rpm of stirrer speed. After the reaction is complete, the product will need to be separation using separation funnel, then centrifuge then rotary to remove any excess catalyst, methanol and water vapour during the experiment is being done. Then it will undergo characterisation process. Characterisation is important to determine the specification of

the product and contain of the produce biodiesel. The characterisation process is through standard method of ASTM to obtain the result.

Chapter 4 will show the result obtain from the experimental product of produced biodiesel from castor oil. This chapter will discuss the result obtain and comparing to other research result on the production of biodiesel produced from castor oil.

Chapter 5 is the final chapter on the conclusion and the recommendation on this paper, and possible future work that could be done on continuing this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This paper presents the experimental studies of biodiesel transesterification process and its characterization. In the transesterification process, a heterogeneous catalyst which is calcium oxide (CaO) use rather than normal homogeneous catalyst. Mixture of methanol-catalyst and oil will be selected and used the best molar ratio for the transesterification process. Production of this transesterification process will lead to production of biodiesel, an alternative to conventional fossil based diesel (Fjerbaek, et. al., 2008). Production of biodiesel using heterogeneous catalyst is less cost as the catalyst efficiency not decrease in large number as usage of heterogeneous catalyst, and will not require additional neutralization process (Romero, et. al., 2011, MacLeod, et. al., 2007). In this experiment, castor oil will be used in the process. Castor oil obtained from extracted castor bean, which contain large percentage of oil.

2.2 Introduction

This paper presents production of biodiesel produced from castor oil through transesterification process by using CaO as catalyst. The produced biodiesel later being characterise to determine either the produced biodiesel is according to the standards.

2.3 Selection of Castor Oil

Castor oil is a product obtained from the extraction of castor bean or also known as castor seed. Scientifically, castor bean named as Ricinus communis L. is a type of plant that belong to Euphorbiacceae family. Castor oil is a type of vegetable oil gained from planted crop and currently widely planted at some countries. The table 2.3-1 shows

different type of oil producing crop and their yield per acre. The advantages of using vegetable oil as sources of fuel are ready availability, renewability and nature-portability. Despite of the advantages, there are also disadvantages such as higher viscosity, the reactivity of the unsaturated carbon chained and lower value of volatility. These disadvantages can be overcome with several methods during the process of producing the biodiesel itself.

Figure 2-3-1: Castor plant

Figure 2-3-2: Castor bean

Table 2.3-1: Edible and non-edible oil producing crops and their yield

Oil Producing Crop/Plant	Yield (Lb Oil/Acre)
Palm	4585
Coconut	2072
Sunflower	734
Soybean	344
Cottonseed	250
Jatropha	1458
Castor bean	1089
Rubber seed	199

The oil contain from this bean approximately in range of 35% - 55%. This percentage of oil can be consider as high value in number as the oil is extracted from bean itself, depending on the environment the seed being planted. With high contain of

ricinoleic acid, a monounsaturated with 18-carbon fatty acid and hydroxyl group on the twelfth carbon, up to 90%, this make the castor oil become one of most valuable chemical feedstocks nowadays (Chakrabarti and Ahmad, 2008).

Table 2.3-2: Fatty acid composition of castor oil (Conceicao, et. al., 2007)

Fatty Acid	Composition (%)
Ricinoleic Acid	90.2
Linoleic Acid	4.4
Oleic Acid	2.8
Estearic Acid	0.9
Palmitic Acid	0.7
Dihidroxiestrearic Acid	0.5
Licosanoic Acid	0.3
Linoleic Acid	0.2

Based on table 2.3-2, Conceicao, et. al., show that ricinoleic acid is the highest acid contain in the castor oil. Other acid such as linoleic, oleic, estearic, palmitic, dihidroxiestrearic, licosanoic and linoleic only contain less than 5% of the total composition inside the castor.

By containing high value of ricinoleic acid and hydroxyl group, is another reason why castor oil has high viscosity and density (Scholz and da Silva, 2008). Researcher start focus to castor oil due on advantages given by the oil itself. Transesterification of castor oil is characterized by its stability and solubility which affect the reaction. Furthermore, this oil favour the transesterification as it soluble in the methanol. Results obtained by previous researcher showed that temperature slightly affect the reaction, but the catalyst amount affect more specifically (de Lima de Silva et. al., 2009).

Since almost more than 95% of biodiesel create from edible oil, as castor is one type oil plant which produce edible oil, converting these type of oil into biodiesel also mean creating new alternative automotive fuel. Although this is one of positive to create better future, this also will bring negative issue to the earth as when the large-production

of edible could bring global imbalance between the food supply and market demand. People more tend to compete to joint into the market demand rather than food supply because more profit could be gain in this situation. More destruction and deforestation could happen and the forest being cleared to create oil crop plantation purpose. Due to this issue can bring us into depletion of edible oil supply around the world in exchange of biodiesel production as the substitute fuel (Deligiannis, et. al).

2.4 Biodiesel and Transesterification Process

Biodiesel is one type biofuel which getting high demand, due to depleting volume of fossil fuel left inside the earth. Recently, the prices of crude oil keep hiking, and environmental concern make biodiesel became major focus to many researcher. Biodiesel can be produced from renewable biological sources such as vegetable oil and animal fats. Rudolf Diesel was the first one to test peanut oil as fuel for his engine about hundred years ago. In order to produce biodiesel, there are four methods to reduce the high viscosity of vegetable oils that are blending with petrodiesel, pyrolysis, microemulsification and transesterification (Gerpen and Knothe, 2005). Biodiesel can be produced from various type of vegetable oil such as palm oil, coconut oil, sunflower, soybean, rubber, etc. Special interest shown to vegetable oil because it reduce particulate emission relatively compare to petroleum diesel (Sreenivas, et. al., 2011). Petroleum diesel or diesel engine is one of major air pollutant. This could affect the ozone layer and give the greenhouse effect. Carbon monoxide produced from exhaust emission could lead to hypoxia and causes further health effect. Hydrocarbon emission are carcinogenic, odorants and irritant, while nitrogen oxide could cause pulmonary diseases.

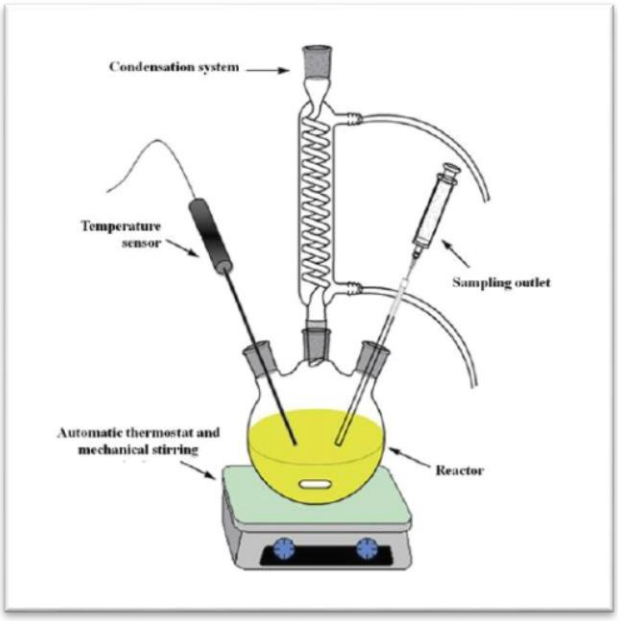

Figure 0-3: Illustration of apparatus set-up of experimental transesterification system (Encinar, et. al., 2010)

In this research, transesterification method will be used as the reaction lead to production of biodiesel. Commonly, this process prepared product of methyl esters because the methanol is the cheapest among other type of alcohol. Basically, the general reaction of this reaction is when the oil is mixed with alcohol, then it will produce alkyl ester and glycerol. The alkyl ester is the desired product which is biodiesel itself. Generally, transesterification process can be done with help of either acid or base catalyst.

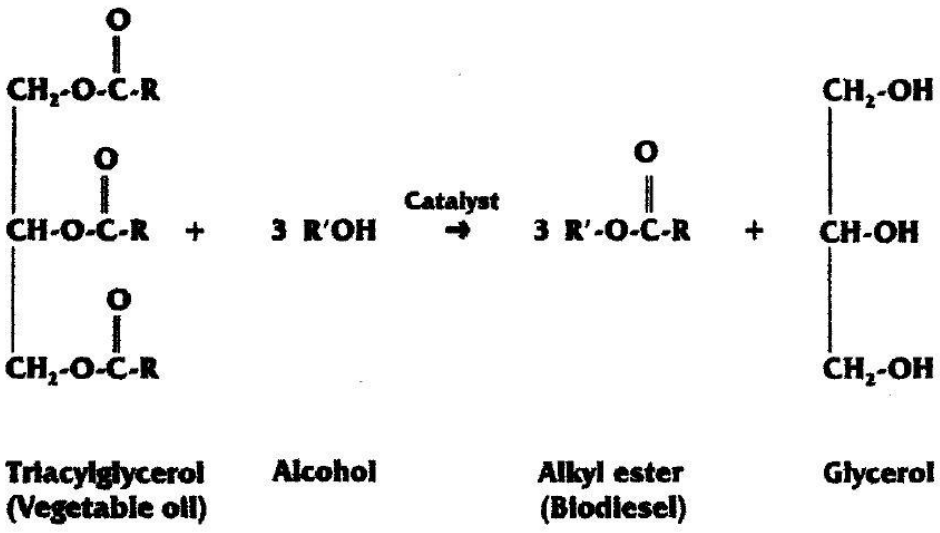

Figure 2-4-4: Transesterification process reaction

2.5 Catalyst

Presence of catalyst during the transesterification process is very essential to increase the rate of reaction. Currently, most of biodiesel produced are using homogeneous catalyst. The fact that homogeneous catalyst cannot be reused is the major disadvantage and reduce the efficiency of the transesterification process. Due to this problem, an addition and further washing stage need to imply, where an additional cost will be needed from the production cost. An approach by using heterogeneous has been done, but despite of all effort, the heterogeneous catalyst for the biodiesel production still have not use at industry level yet. This research will introduce the usage of a type of heterogeneous catalyst which is calcium oxide (CaO). The heterogeneous acid and basic catalyst can be classified as Bronsted or Lewis catalysts, where its character will determine the transesterification reaction rate (Romero et al., 2011). Various research has been done determined that different catalyst used will need different parameter such as catalyst weight and temperature, which affect the final result of the experiment and the production of biodiesel.

2.6 Characterisation

To make sure the product can be use and blend normally, it must be characterise and follow the standards. The importance of characterisation is to determine contain and the specification of the oil produced. There are a lot of standard set by the standards council and almost every country have their own standards. ASTM D6751 has been choose to be reference in this thesis. In the ASTM D6751 standards, several specification are being highlighted to ensure the produced biodiesel can be use and blend with petrodiesel. In this thesis, only several major specification highlighted due to time constraint and based on the availability of the test equipment inside the laboratory.

Figure 2-6-5: Table of ASTM D6751 standards

Biodiesel Standards		USA
Specification		ASTM D 6751-07b
Applies to		FAAE
Density 15°C	g/cm³	
Viscosity 40°C	mm²/s	1.9-6.0
Distillation	% @ °C	90%,360°C
Flashpoint (Fp)	°C	93 min
CFPP	°C	
Cloud point	°C	* report
Sulphur	mg/kg	15 max
CCR 100%	%mass	0.05 max
Carbon residue (10%dist.residue)	%mass	
Sulphated ash	%mass	0.02 max
Oxid ash	%mass	
Water	mg/kg	500 max
Total contamination	mg/kg	
Cu corrosion max	3h/50°C	3
Oxidation stability	hrs;110°C	3 hours min
Cetane number		47 min
Acid value	mgKOH /g	0.5 max
Methanol	%mass	0.2 max or Fp <130°C
Ester content	%mass	
Monoglyceride	%mass	
Diglyceride	%mass	
Triglyceride	%mass	
Free glycerol	%mass	0.02 max
Total glycerol	%mass	0.24 max
Iodine value		
Linolenic acid ME	%mass	
C(x:4) & greater unsaturated esters	%mass	
Phosphorus	mg/kg	10 max
Alkalinity	mg/kg	
Gp I metals (Na,K)	mg/kg	5 max
GpII metals (Ca,Mg)	mg/kg	5 max
PAHs	%mass	
Lubricity / wear	µm at 60°C	

2.7 Summary

This thesis will proved that the usage of heterogeneous catalyst during transesterification process will produce biodiesel according to standards. Besides, castor oil also can be a major source in producing biodiesel, as substitute for petrofuel in the future.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Overview

In this thesis, transesterification process is the major process use in the experiment. The ratio of methanol-catalyst and oil used is 6:1 ratio, as be found the best ratio suggested in producing castor oil. The reaction will be done in a batch reactor for several hours, then later separated in a separation funnel. The unused catalyst will later be removed and oil will be centrifuged before rotary to ensure the biodiesel produced are free from any unwanted component and only pure biodiesel will be kept.

3.2 Introduction

In this experiment, the best value for the methanol-catalyst and oil ratio will be obtained. The important to find the exact ratio is to maximize the efficiency of the process. The high efficiency of the process means the more to perfect process we could obtained from the experiment and faster the reaction will be react. To run in small scale experimental test, the raw feedstock which is castor oil will be mix with the mixture of methanol and catalyst inside a reactor, then being left for couple of hours to ensure the reaction is completely react. When the reaction complete, the product will be left in a separation funnel for a night to separate the catalyst and produced oil. After the separation, the oil centrifuged to remove any excess catalyst inside the oil then later rotary to remove any excess methanol or water vapour.

3.3 Chemicals

Chemicals use in this study will be obtained from University Malaysia Pahang Chemical Engineering Laboratory. Alcohol that will be used for the transesterification process is methanol, while the catalyst that is calcium oxide also will be gained from the laboratory.

3.4 Castor Oil

Castor oil is a type of oil can be get by extracting the castor bean. Due to time constraint based on provided time on conducting this experiment, castor oil will be bought from the market to save time, and the grade of castor oil used was only technical grade oil, not purified castor oil.

3.5 Production of Biodiesel through Transesterification Reaction

The transesterification process of this experiment was done by using 6:1 methanol-catalyst and oil ratio. This ratio proven as the best ratio in producing biodiesel from vegetable oil feedstock. The feedstock oil used in this experiment is castor oil. Castor oil is one type of oil which very viscos due to high number of carbon chain. From 6:1 methanol-catalyst and oil molar ratio, the volume of castor oil, methanol and catalyst used being calculated. The catalyst used is only 1% weight of total mass of methanol and castor oil.

The reactor used in this experiment is round glass reactor, attach with thermometer to ensure inside reactor temperature and stirrer. This reactor is set-up in a fume hood, due to reactive material which was methanol is being used in this experiment. The oil inserted into the reactor with stirrer speed of 200rpm and the reactor was heated up to 100^{o}C to remove and excess water or vapour inside the oil because the oil used in this experiment was technical oil, and the oil was kept inside air-conditioning room, considering the cold air will cause production of water inside the oil storage. After the oil heated to remove the excess water, the methanol and catalyst mixed to obtained methanol-catalyst mixture before pour into the reactor. The stirrer speed was maintain at 200rpm while the reaction temperature was maintain at 65-68^{o}C. Then the